Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Molecular Dynamics Simulations

S1. Silica Pore Geometry and Surface Chemistry

The cylindrical amorphous silica nanopore used in this study was generated using the PoreMS framework[53]. The pore was carved from an atomistically detailed amorphous silica matrix and subsequently hydroxylated using the internal reconstruction protocol implemented in PoreMS. Surface binding sites that could not be assigned to a specific local coordination motif were automatically converted into silanol groups or siloxane bridges.

The pore has a nominal diameter of 2.4 nm and a length of approximately 12.2 nm along the pore axis (z-direction). Periodic boundary conditions were applied along the pore axis, while confinement in the transverse (x,y) directions is provided by the surrounding silica matrix. All silica atoms were kept frozen during the simulations.

The accessible pore volume is $V_{pore} = 54.158 nm^3$ with an internal surface area of 90.37 nm^2. The surface contains both single silanol (SL) and geminal silanol (SLG) groups, resulting in a hydroxylation density of approximately 6.04 $\mu mol m^{-2}$, consistent with experimentally reported values for hydroxylated amorphous silica surfaces[74,75].

Table S1: Geometric and surface-chemical characteristics of the 2.4 nm silica nanopore used in the MD simulations.

Quantity	Value
Pore diameter (nm)	2.397
Pore length (nm)	12.245
Accessible pore volume (nm^3)	54.158
Internal surface area (nm^2)	90.371
Single silanol groups (SL)	293
Geminal silanol groups (SLG)	18
Siloxane bridges (SLX)	78
Total OH groups	329
Hydroxylation ($\mu mol m^{-2}$)	6.045

Quantity	Value
Silica framework	Frozen

S2. Experimental Bulk Densities and Bulk MD Validation

Experimental bulk densities for pure acetone, pure cyclohexane, and their binary mixtures at 298 K were taken from standard literature sources. Corresponding bulk MD simulations were performed using identical force-field parameters and temperature conditions as for the confined systems in order to validate the force-field description of bulk thermodynamic properties.

For all systems considered, MD-derived bulk densities agree with experimental values within approximately 1-2 % as shown in Table S2, confirming that the employed force-field combination provides an adequate description of bulk thermodynamic properties. As the force fields used are primarily optimized for static properties, bulk density constitutes the primary benchmark for validation, whereas dynamical properties are not expected to be quantitatively accurate.

Table S2. Comparison of experimental bulk densities and densities obtained from bulk MD simulations for pure liquids and acetone-cyclohexane mixtures at 298K

System	$\rho_{exp}\ (kgm^{-3})$	$\rho_{MD}\ (kgm^{-3})$	Reference
Acetone	785.5	784.3	76,77
Cyclohexane	772.9	772.4	76,77
Cyclohexane–Acetone (50/50)	763.8	762.4	77

S3. Density-Based Determination of Molecule Numbers

For the confined systems, the number of liquid molecules inserted into the nanopore was chosen such that the average density within the accessible pore volume matches the experimental bulk density of the corresponding pure liquids or mixtures.

For a pure liquid of density ρ and molar mass M filling a pore of volume V, the number of molecules N is given by

$$N = \frac{\rho V}{M} N_A,$$

where N_A is Avogadro's number.

For binary mixtures with mole fraction x, the mixture density was approximated by ideal mixing of specific volumes,

$$\frac{1}{\rho_{mix}} = \frac{x_1}{\rho_1} + \frac{1 - x_1}{\rho_2},$$

and the total number of molecules in the pore was obtained accordingly. All molecule numbers were rounded to the nearest integer.

S4. Ideal and Actual Molecule Numbers in the 2.4 nm Pore

Table S3 lists the ideal total molecule numbers obtained from bulk-density matching for all systems simulated in the 2.4 nm silica nanopore, together with the total molecule numbers used in the MD simulations. In all cases, the MD systems contain fewer molecules than the ideal bulk-density estimate. This reflects confinement-induced density inhomogeneities, including excluded-volume effects near the silica surface and reduced density in the pore center.

Absolute densities in confinement are therefore not expected to match bulk values. Importantly, the same density-matching procedure was applied consistently to all systems, ensuring comparable relative densities across all investigated compositions.

Table S3. Ideal total molecule numbers for the simulated systems in the 2.4 nm silica nanopore based on bulk or bulk-mixture density compared to the total molecule counts used in MD simulations. The deviation is defined as $(N_{total}(MD) - N_{total}(ideal))/N_{total}(ideal) * 100$.

System	$x_{ace}(MD)$	$N_{total}(ideal)$	$N_{total}(MD)$	Deviation (%)
Pure acetone	1.000	441	437	-0.91
Pure cyclohexane	0.000	302	275	-8.94
50/50 ACE-CHX	0.492	366	360	-1.64
10/90 ACE-CHX	0.095	312	305	-2.24

S5. Summary of MD Simulation Parameters

All MD simulations were performed using GROMACS 2023 with a timestep of 1 fs. Confined systems were equilibrated in the canonical (NVT) ensemble at 300 K using the Nosé-Hoover thermostat, followed by 100 ns production runs in the NVT ensemble. Bulk systems were equilibrated in the isothermal–isobaric (NPT) ensemble at 300 K and 1 bar prior to NVT production runs. Long-range electrostatics were treated using the particle-mesh Ewald method, and all bonds involving hydrogen atoms were constrained using the LINCS algorithm. Trajectory coordinates were saved every 1 ps.

S6. Residence-Time Analysis at Extended Adsorption Threshold

To assess the robustness of the residence-time analysis with respect to the definition of the adsorption region, additional calculations were performed using larger cutoff distances, $r_{thresh} = 5.0$ Å and 6.0 Å, in addition to the primary threshold of 4.0 Å used in the main text. The survival probability, P(t), was computed using the same multiple–time–origin (MTO) first-passage formalism described in the main article. Figure 12 display the P(t) curves for these extended thresholds

At $r_{thresh} = 5.0$ Å, the survival probabilities still retain qualitative distinctions between acetone and cyclohexane. However, there is a visible increase in the long-time plateau, reflecting the inclusion of more weakly bound and near-surface molecules beyond the first adsorbed layer.

At larger thresholds $r_{thresh} = 6.0$ Å, the decay of P(t) becomes significantly slower, and the curves are increasingly dominated by geometric confinement within the pore rather than genuine surface adsorption. At this distance, the survival probability primarily tracks the overall residence within the pore volume, making it difficult to extract a clear physical interpretation regarding specific interfacial binding.

These observations confirm that $r_{thresh} = 4.0$ Å, corresponding to the first adsorption layer identified from radial density profiles, provides the most physically meaningful definition of interfacial residence.